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# Significant structure theory and thermodynamic properties of liquid carbonyl fluoride and trifluorophosphine

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The significant structure theory has been used to evaluate the thermodynamic properperties of the liquid carbonyl fluoride and trifluorophosphine Since the entropy of fusion in the case of trifluorophosphine was found to be 1.837 e u., free rotation was assumed even in the solid state Hence for the 12 degrees of freedom for this molecule three were assigned for rotation three for translation and six for vibrations In the case of carbonyl fluoride the entropy of fusion is very large (9 903 e u ) and hence no rotation was assumed in the solid state Out of the 12 degrees of freedom the solid like part was treated as a six degree Einstein oscillator with the remaining six degrees as vibrations for this molecule The calculated properties like molar volumes, vapour pressures and entropies which involve the first derivatives of the partition function are in good agreement with experiment. Properties like thermal expansion coefficient, isothermal compressibility and heat capacities which involve the second derivatives of the partition function are also in satisfactory agreement with experiment. This shows that the partition function formulated on the basis of the significant structure theory for the two liquids investigated adequately represents the liquid state properties of the molecules.

## Introduction

The liquids carbonyl fluoride and trifluorophosphine have been investigated thermodynamically by Pace & Reno (1968), and Pace & Petrella (1962) respectively. The entropy of fusion was found to be 1.837 e.u. in the case of trifluorophosphine and 9.903 e. u. in carbonyl fluoride. The entropy of fusion was found to be very nearly equal to the so-called Communal Entropy which is nearly equal to $R$. Hence free rotation in the case of solid trifluorophosphine is assumed. In the case of carbonyl fluoride the entropy of fusion being very large no rotation is assumed in the solid state. Therefore it is important to study these two different molecules with very different entropies of fusion. We report here the thermodynamic properties as derived from the significant structure theory developed by Eyring and his collaborators (1948, 1962, 1966).

According to this theory the liquid is assumed to possess vacancies of molecular size which confer gas-like properties on a neighbouring molecule jumping into the holes and hence a solid-like molecule acquires positional degeneracy equal to the number of neighbouring vacancies. Assuming random distribution of vacancies the mole fractions of gas-like and solid-like molecules are $(V-V_s)/V$ and $V_s/V$ respectively. Here $V$ and $V_s$ are the molar volumes of the liquid and reference solid respectively.

*Phosphorous trifluoride* (*Trifluorophosphine* $PF_3$)

Out of 12 degrees of freedom for this tetra-atomic molecule three were assigned to rotation, three for translation and six for vibration. Thus the partition function for liquid trifluorophosphine becomes

$$f_{PF_3} = \left[ \frac{e^{Es/RT}}{(1-e^{\theta/T})^3} \frac{\pi^{\frac{1}{2}}}{\sigma} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A I_B I_C)^{\frac{1}{2}} \prod_{i=1}^{6} (1-e^{-h\nu_i/kT})^{-1} \{1+n(x-1)e^{-w}\} \right]^{N/x}$$

$$\left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{\pi^{\frac{1}{2}}}{\sigma} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A I_B I_C)^{\frac{1}{2}} \prod_{i=1}^{6} (1-e^{-h\nu_i/kT})^{-1} \frac{eV}{N} \right]^{N(1-1/x)} \quad \ldots \quad (1)$$

Here $x = V/V_s$, $\theta$ is the characteristic temperature of the liquid, $\sigma$ is the so-called symmetry number which in the present case is equal to 3, $w = \dfrac{aE_s}{RT(x-1)}$ and $\nu_i$ are the characteristic fundamental vibrational frequencies (Pace *et al* 1962) and the rest of the symbols have their usual statistical mechanical significance. The parametric values $n$, $a$, $\theta$ $V_s$ and $E_s$ are determined according to Chang's method (Rao & Swamy 1970). While adopting this method $E_s$ value is varied so as to give the best fit at the melting point. The values so found are : $n = 11.604$, $a = 7.5963 \times 10^{-4}$, $E_s = 4249.2$ cal/mol, $V_s = 47.394$ cc/mol, $\theta = 75.56°K$.

*Carbonyl fluoride* ($COF_2$) :

As pointed out already this substance has a high entropy of fusion (9.903 e.u.) which indicates that there is no free rotation at all in the solid state. Hence out of the 12 degrees of freedom the solid like part is treated as a six degree Einstein oscillator with the remaining six degrees as vibrations. The characteristic vibration frequencies are taken from Pace & Reno (1968). Thus the partition function for liquid carbonyl fluoride can be written as

$$f_{COF_2} = \left[ \frac{eE_s/kT}{(1-e^{-\theta/T})^6} \prod_{i=1}^{6} (1-e^{-h\nu_i/kT})^{-1} \{1+n(x-1)e^{-w}\} \right]^{N/x}$$

$$\left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{\pi^{\frac{1}{2}}}{\sigma} \left( \frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_A I_B I_C)^{\frac{1}{2}} \prod_{i=1}^{6} (1-e^{h\nu_i/kT})^{-1} \frac{eV}{N} \right]^{N(1-1/x)} \quad \ldots \quad (2)$$

Here the symmetry number of the molecule is 2 and the rest of the symbols have been explained already. The parametric values so found are : $n = 11.07$, $a = 2.5484 \times 10^{-3}$, $E_s = 5739$ cal/mol, $V_s = 53.931$ c.c./mol , $\theta = 45.653°K$.

## Evalution of Thermodynamic Properties of the Liquids from the Partition Function

The Helmholtz free energy $A$ is related to the partition function by the well known equation

$$A = -kT \ln f \quad \ldots \quad (3)$$

Hence from equations 1 and 2 we get

$$A = \frac{RT}{x}(\lambda_1+\lambda_2)-RT(1-1/x)(\lambda_3+\ln x) \tag{4}$$

Here

$$\lambda_1^{PF_3} = \frac{E_s}{RT}-3\ln(1-e^{-\theta/T})+\ln f_{rot}^{PF_3}-\ln f_{vib}^{PF_3} \tag{5}$$

$$f_{rot}^{PF_3} = \frac{\pi^{\frac{1}{2}}}{3}\left(\frac{8\pi^2 kT}{h^2}\right)^{3/2}(I_A I_B I_C)^{\frac{1}{2}} \quad \ldots \tag{6}$$

$$f_{vib}^{PF_3} = \prod_{i=1}^{6}(1-e^{-h\nu_i/kT})^{-1} \quad \ldots \tag{7}$$

$$\lambda_2^{PF_3} = \ln[1+n(x-1)e^{-w}] \quad \ldots \tag{8}$$

$$\lambda_3^{PF_3} = \left\{\frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)+\frac{3}{2}\ln\left(\frac{8\pi^2 kT}{h^2}\right)+\tfrac{1}{2}\ln(I_A I_B I_C)+\tfrac{1}{2}\ln\pi-\ln\sigma - \sum_{i=1}^{6}\ln(1-e^{-h\nu_i/kT})+\ln\frac{eV_s}{N}\right\} \quad \ldots \tag{9}$$

While in the case of $COF_2$ we have

$$\lambda_1^{COF_2} = \frac{E_s}{RT}-6\ln(1-e^{-\theta/T})-\sum_{i=1}^{6}\ln(1-e^{-h\nu_i/kT}) \tag{10}$$

while in the case of carbonyl fluoride similar equations as given in (8) and (9) hold good for $\lambda_2^{COF_2}$ and $\lambda_3^{COF_2}$. Remembering that $P = -(\partial A/\partial V)_T$ the Helmholtz free energy is plotted for a given temperature as a function of volume. The volumes at the points of common tangency are the volumes of the corresponding phases and the vapour pressure is given by the slope of the tangent Except at the triple point a tangent has at most two points of tangency (Eyring *et al* 1964). The volumes and vapour pressures so evaluated are given in tables 1 and 2, and are compared with observed values of Pace & Petrella (1962) and Pace & Reno (1968). A curve of the vapour pressure *versus* temperature is shown in figure 1.

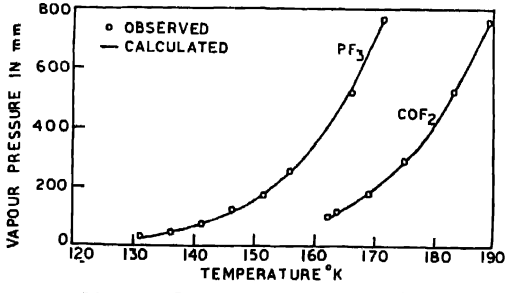


Figure 1. Vapour pressure *vs* temperature.

Table 1. Calculated and observed thermodynamical properties of liquid trifluorophosphine

| Temp°K | Volume cc/mole | Vapour pressure in mm | $-A/RT$ | $S$ cals/mole-deg | $\alpha \times 10^3$ deg$^{-1}$ | $\beta \times 10^6$ atm$^{-1}$ | $C_V$ cals/mole-deg | |
|---|---|---|---|---|---|---|---|---|
| 131 | 49 811 | 22.201 | 27.3481 | 32.5942 | 1.9806 | 87.518 | 12 6051 | Calc |
| | 49.223 | 27 001 | — | — | 2 5268 | — | — | Obs |
| 136 | 50.24 | 39.521 | 26.9254 | 33 2371 | 1.9318 | 90.766 | 12.7343 | Calc |
| | 50.773 | 44 605 | — | — | 2 5707 | — | — | Obs |
| 141 | 50 716 | 67 315 | 26.544 | 33.8823 | 2.0957 | 104.67 | 12.8273 | Calc |
| | 51 006 | 71 561 | — | — | 2.6125 | — | — | Obs |
| 146 | 51.566 | 109.86 | 26 1997 | 34.6747 | 2.2292 | 118 34 | 12.9400 | Calc |
| | 51 10 | 111.58 | — | — | 2.6368 | — | — | Obs |
| 151 | 51.85 | 172.57 | 25.8882 | 35 1853 | 2.1255 | 120.82 | 13.0156 | Calc |
| | 52 79 | 169.04 | — | — | 2 6923 | — | — | Obs |
| 156 | 52.608 | 262.79 | 25.6068 | 35 8731 | 2.5758 | 157.11 | 13 0953 | Calc |
| | 53.496 | 250.49 | — | — | 2 725 | — | — | Obs |
| 166 | 54.03 | 557.83 | 25.1228 | 37.3014 | 2 5777 | 181.29 | 13 6176 | Calc |
| | 54.97 | 517.0 | — | — | 2.8016 | — | — | Obs |
| 171.77 | 54 504 | 795.5 | 24.9488 | 3779648 | 2.6239 | 190.86 | 13.8663 | Calc |
| | 55.793 | 760 | — | 38.041 | 2 8675 | — | — | Obs |

Table 2 Calculated and observed thermodynamical properties of liquid carbonyl fluoride

| Temp°K | Volume cc/mole | Vapour pressure in mm | $-A/RT$ | $S$ cals/mole-deg | $\alpha \times 10^3$ deg$^{-1}$ | $\beta \times 10^6$ atm$^{-1}$ | $C_V$ cals/mole-deg | |
|---|---|---|---|---|---|---|---|---|
| 161 89 | (58 46) | (93.75) | 26.1275 | 29.7296 | 3.2269 | 161.26 | 14.9706 | Calc |
| (M.P.) | 58 46 | 93.75 | — | 29.730 | 3.7198 | — | — | Obs |
| 163.6 | 58.89 | 110 04 | 26 0429 | 30.0633 | 2.9995 | 156.35 | 15.0601 | Calc |
| | 58.836 | 109 60 | — | — | 3 7403 | — | — | Obs |
| 169 | 60.187 | 177.21 | 25 6969 | 41 0058 | 2.9105 | 170.58 | 15.0031 | Calc |
| | 60.05 | 178.6 | — | — | 3.8123 | — | — | Obs |
| 174.94 | 61.373 | 286.54 | 25.3595 | 31.9082 | 3.1232 | 200.98 | 15.6516 | Calc |
| | 61.443 | 289.89 | — | — | 3.914 | — | — | Obs |
| 182.9 | 61.697 | 510 98 | 24.9613 | 32.5632 | 2.9657 | 197.02 | 16.2235 | Calc |
| | 63.419 | 520 16 | — | — | 4.1479 | | — | Obs |
| 188.58 | 62.669 | 741.45 | 24.7097 | 33.2844 | 3.1843 | 226.46 | 16.5769 | Calc |
| (B.P.) | 64.91 | 76.0 | — | 33.777 | 4.2779 | — | — | Obs |

### Entropy of vaporization

Molar entropies of the liquid are calculated from the well known equation

$$S = -(\partial A/\partial T)_V. \qquad \ldots (11)$$

The values so calculated are given in the two tables in columns 5 for trifluorophosphine and carbonyl fluoride respectively. The entropy of vaporization is determined as the difference in the entropy of the gas and liquid and the values are :

| | | | |
|---|---|---|---|
| $PF_3$ | at 171.77°K | 20.4102 (Cal) | 20.289 (obs) |
| $COF_2$ | at 188.58°K | 23.9970 (Cal) | 23.17 (obs) |

### Compressibility the liquids

The isothermal compressibility is given by

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V\left(\frac{\partial^2 A}{\partial V^2}\right)} \qquad \ldots (12)$$

Further we have $P = -(\partial A/\partial V)_T$. Hence from equation (4) we get

$$P = \frac{RT}{V_s x^2}\left[-(\lambda_1+\lambda_2)+x\left(\frac{\partial \lambda_2}{\partial x}\right)_T+\lambda_3+\ln x+x-1\right] \qquad \ldots (13)$$

Hence we have for the isothermal compressibility of the liquid

$$\frac{1}{\beta} = \frac{-RT}{V_s x^2}\left[x^2\frac{\partial^2\lambda_2}{\partial x^2}-2x\left(\frac{\partial \lambda_2}{\partial x}\right)_T+2\lambda_2-x+3-2(\lambda_3+\ln x-\lambda_1)\right] \qquad \ldots (14)$$

This will form a severe test of the partition function since it involves the second derivatives. The values calculated from equation (14) are given in the tables in columns 7 for trifluorophosphine and carbonyl fluoride respectively.

By definition

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial^2 A}{\partial V \partial T}\right)\Big/\left(\frac{\partial^2 A}{\partial V^2}\right) = \beta\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (15)$$

Hence from equation (13) we get

$$\frac{\partial P}{\partial T} = \frac{R}{V_s x^2}\left[-(\lambda_1+\lambda_2)+x\left(\frac{\partial \lambda_1}{\partial x}\right)+\lambda_3+\ln x+x-1-T\left(\frac{\partial \lambda_1}{\partial T}\right)-T\left(\frac{\partial \lambda_2}{\partial T}\right)\right.$$
$$\left.+x\left\{\frac{\partial}{\partial T}\left(\frac{\partial \lambda_2}{\partial x}\right)_T\right\}_V+T\frac{\partial \lambda_3}{\partial T}\right] \qquad \ldots (16)$$

The calculated and observed values are given in table 1 and 2 column 6 for trifluorophosphine and carbonyl fluoride respectively.

The heat capacity at constant volume is given by

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{R}{x}\left[2T\left(\frac{\partial \lambda_1}{\partial T}\right)_x + T^2\left(\frac{\partial^2 \lambda_1}{\partial T^2}\right)_x + 2T\left(\frac{\partial \lambda_2}{\partial T}\right)_x + T^2\left(\frac{\partial^2 \lambda_2}{\partial T^2}\right)_x\right]$$

$$-R(1-1/x)\left[2T\left(\frac{\partial \lambda_3}{\partial T}\right)_x + T^2\left(\frac{\partial^2 \lambda_3}{\partial T^2}\right)_x\right] \qquad (17)$$

and the values obtained are shown in column 8 of the tables.

## Discussion

In both the above liquids, the calculated and observed volumes, vapour pressures and entropies agree very well The calculated properties like thermal expansion coefficient, isothermal compressibility and heat capacities are also in satisfactory agreement with experiment thereby proving that the partition functions formulated adequately represent the liquid state of the two molecules.

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